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The available invention concerns an improved process to the preparation of Epoxiden from Olefinen and hydrogen peroxide using an oxidation catalyst on basis of titanium or Vanadiumsilikaliten with zeolite structure.

Methods to the preparation of Epoxiden from Olefinen and aqueous hydrogen peroxide using Titansilikaliten as Epoxidierungskatalysatoren are from the EP-A 100,119 (1) and the USA 5,384,418 and/or. The USA 5,463,090 (2) known.

In accordance with (1) the Epoxidierung of ethyls, propen, allyl chloride, 2-Buten, 1-Octen, 1-Tridecen, Mesityloxid, Isopren, Cycloocten and Cyclohexen becomes by means of 36 gew. - % igem aqueous H<sub>2</sub>O<sub>2</sub> in presence of a Titansilikalits, which in powdered form or with a particle size distribution from 25 to 60 mesh (a corresponding filter mesh size from 0.25 mm to approx. 0.7 mm) is present autoclaves a conducted.

Out (2) is known that one can use Titansilikalite, which can be present as powders, spheres, Extrudate or Monolithe in combination with special Anthrahydrochinon/Anthrachinon Redoxsystemen for the Epoxidierung of Olefinen such as propen by means of oxygen, which is converted intermediately to H<sub>2</sub>O<sub>2</sub>. The Titansilikalite can do 1 to 99 Gew. - % at binding agents such as silicon or alumina contained.

Such Epoxidierungsverfahren known from the state of the art exhibits however disadvantages. With use of not formed Epoxidierungskatalysatoren as in (1) these are too fine-grained, so that they cause mechanical problems, for example with D separation. Also the use of additional auxiliary agents is often unwanted like the Anthrahydrochinon/Anthrachinon Redoxsysteme in (2), since such auxiliary agents cause additionally costs and expenditure.

Task of the available invention was it to make simple and efficient Epoxidierungsverfahren available of Olefinen which does not exhibit the disadvantages of the state of the art any longer.

A method was found accordingly to the preparation by Epoxiden from Olefinen and hydrogen peroxide using an oxidation catalyst on basis by titanium or Vanadiumsilikaliten with zeolite structure and in absence of a Anthrahydrochinon/Anthrachinon Redoxsystems, which is characterized by the fact that the oxidation catalyst by solidifying shaping processes formed is.

As solidifying shaping processes in principle all methods can be used for the corresponding figuration, how with catalysts general are usual. Preferred ones become processes, with those the shaping by extruding in usual Extrude for example strands with a diameter from usually 1 to 10 mm, in particular 2 to 5 mm, made. If binding agents and/or auxiliary agents become required, the extruding appropriately a mixture or a kneading process is upstream. If necessary made after the extruding still another calcining step. The obtained strands become preferably gewünschtenfalls zerklein granulates or split with a particle diameter from 0,5 to 5 mm, in particular 0.5 to 2 mm. This granulates or these split and also other pathways generated catalyst molded articles of contained practically no fine-more granular portions than such with 0.5 mm of minimum particle

diameters.

In a preferable embodiment the used formed oxidation catalyst up to 10 Gew contains. - % binding agent, related to the total weight of the catalyst. Particularly preferred Bindemittelgehalte are 0.1 to 7 Gew. - %, in particular 1 to 5 Gew. - %. As binding agents in principle all compounds used for such purposes are suitable; preferred become compounds, in particular oxides, the silicon, aluminum, boron, phosphorus, zirconium and/or titanium. Of particular interest as binding agents is silica, whereby the  $\text{SiO}_2$  can become as Kieselsol or introduced in the form of Tetraalkoxysilanen into the shaping step. Also as binding agents oxides of the magnesium and beryllium as well as clays, z are more useful. B. Montmorillonite, Kaoline, Bentonite, Halloysite, Dickite, would NAK-guess/advise and Anaxite.

As auxiliary agents for the solidifying shaping processes for example amplifier rank aids for the extruding are to be called, a usual amplifier rank aid are methyl cellulose. Such agents are usually burned in a following calcining step completely.

The so prepared formed oxidation catalysts exhibit a high measure-specific activity and for all conversion driving fashions and reactor types sufficient hard ones and abrasion resistance.

The described formed oxidation catalysts are in principle known from the writing (2).

The formed oxidation catalysts are based on titanium or Vanadiumsilikaten with zeolite structure. Zeolites are known-measured crystalline Alumosilikate with ordered channel and cage structures, whose pore openings lie within the range of micropores, which are smaller than 0.9 Nm. The network of such zeolites is constructed from  $\text{SiO}_4$  and  $\text{AlO}_4$ -Tetraedern, which are connected by in accordance with one oxygen bridges. A review of the known structures is for example with W.M. Meier and I.E. Olson, ?Atlas OF Zeolite Structure of type?, Butterworth, 2nd OD., London 1987.

There is now also zeolites known, which no aluminum contained and titania partial with those in the silicate lattice in place of Si (IV) stands as Ti (IV). These titanium zeolites, in particular such with a crystal structure from the MFI type, as well as possibilities to their preparation are described, for example in the EP-A 311,983 or the EP-A 405,978. Except silicon and titanium such materials know also additional elements such as aluminum, zirconium, tin, iron, cobalt, nickel, gallium, boron or small amounts at fluorine contained.

In the described oxidation catalyst the titanium of the zeolite can be partial or complete by vanadium replaced. There molecular ratio from titania and/or vanadium to the sum from silicon plus titania and/or vanadium usually lies within the range of 0,01: 1 to 0,1: 1.

Titanium zeolites with MFI structure are known for the fact that them  $\text{cm}^{-1}$  over a particular pattern with the determination of their Roentgen diffraction photographs as well as additionally over a stand oscillation gang within the infrared range (IR) with approximately 960;  $-1$  to be identified can differ and thereby from alkali metal titanates or crystalline and amorphous  $\text{TiO}_2$ -Phasen.

Typically one manufactures the titanium mentioned and also vanadium zeolites by the fact that one an aqueous mixture from a  $\text{SiO}_2$ -Quelle, a titanium and/or. Source of vanadium such as titania and/or. a corresponding vanadium oxide and a nitrogenous organic cousin (?template compound?), z. B. Tetrapropylammoniumhydroxid, if necessary still under adding alkali metal compounds, in a receiver under elevated temperature in the period of several hours or some days converts, whereby the crystalline product develops. This becomes abfiltrie washed, dried and the distance of the organic nitrogen cousin with elevated temperature fired. In the so obtained powder the titanium lies and/or. the vanadium at least partly within the zeolite stand in changing portions with four, five or sixfold co-ordination forwards. To the improvement of the catalytic behavior still another repeated wash treatment with sulfur-sour hydrogen peroxide solution can follow, on which the titanium and/or. Vanadium zeolite powders again dried and fired will must; a treatment with alkali metal compounds can follow, in order to transfer the zeolite v of the H-form into the cation form. The so prepared titanium and/or. Vanadium zeolite powder becomes then described above formed in the sense of the available invention like.

Preferred titanium or vanadium zeolite is such with Pentasil zeolite structure, in particular the types with radiographic association to the BEA, MOR, CLAY/TONE, MTW, FER, MFI, MEL or MFI/MEL

Mischstruktur. Zeolites of this type are for example in W.M. Meier and I.E. Olson, ?Atlas OF Zeolite Structure of type?, Butterworths, 2nd OD., London 1987, described. More conceivable further titanhaltige zeolites with the structure of the ZSM-48, are ferricguessed/ advised beta ZSM-12, or - zeolite and the mordenite for the available invention.

The invention process to the preparation of Epoxiden can become in principle with all usual conversion driving fashions and in all usual reactor types conducted, for example in suspension driving fashion or in a fixed bed arrangement. One can work continuously or discontinuously. Preferably the Epoxidierung becomes however conducted in fixed bed equipment.

The inventive Epoxidierung becomes appropriately in liquid phase with aqueous hydrogen peroxide, which usually a concentration from 10 to 50 Gew. -, conducted exhibits %. One works favourable-proves at temp advice from -20 to 70 DEG C, in particular -5 to 50 DEG C, at a pressure from 1 to 10 bar and in presence of solvents. As solvents alcohols, z are suitable. B. Methanol, ethanol, isopropanol or third. - Butanol or mixtures from this, and in particular waters. One can use also mixtures of the alcohols mentioned with water.

The used Olefin can be any organic compound, which contains at least an ethylenic insatiated double bond. It can be aliphatic, aromatic or cyclo-aliphatic nature, it can of a linear or a branched structure consist. Preferably the Olefin contains 2 to 30 C-atoms. More than an ethylenic insatiated double bond can be available, so for instance in serving or trienes. The Olefin knows additionally functional group such as halogen atoms, groups of carboxyls, carbon ester functions, hydroxyl groups, Etherbrücken, sulfide bridges, Carbonylfunktionen, Cyanogruppen, Nitrogru or amino groups contained.

Typical examples of such Olefine are ethyls, propen, 1-Buten, cis and trans-2-Buten, 1,3-Butadien, pentenes, Isopren, Hexene, Octene, Nonene, Decene, Undecene, Dodecene, cyclopentene, Cyclohexen, Dicyclopentadien, Methylencyclopropan, Vinylcyclohexan, Vinylcyclohexen, allyl chloride, acrylic acid, Methacrylsäure, Crotonsäure, Vinyllessigsäure, allyl alcohol, alkyl acrylates, Alkylmethacrylate, oleic acid, Linolsäure, Linolensäure, esters and Glyceride of such insatiated fatty acids, styrene, (1-Methylstyrol, Divinylbenzol, Inden and stilbene. Also mixtures of the Olefine mentioned can become after the invention process epoxidized.

The invention process is suitable in particular for the Epoxidierung from propen to propylene oxide.

The invention process to the preparation of Epoxiden as well as the formed oxidation catalysts used therein exhibit a set of advantages. How already mentioned possesses the oxidation catalysts an high measure-specific activity, which decreases in the course of the time not substantially, and a sufficient hard one and abrasion resistance, which makes it interesting in particular for the employment in fixed bed equipments. Because the catalyst molded articles possess no small and kleinstteiligen portions, which influences negative by support effects can exercise are the secondary and decay product spectrum with the Epoxidierung small and an associated activity reduction over the time practically not more detectable.

Also of advantage only the minor proportion at required binding agents is, D. h. maximally 10 Gew. - %, in the formed oxidation catalyst, usually contained such catalysts up to 20 Gew. - % at binding agents. Such high Bindemittelgehalte impair naturally the activity of the catalyst.

Further it is from advantage that no additional cost-intensive or expenditure of causing auxiliary materials must be along-used such as Anthrahydrochinon/ Anthrachinon Redoxsysteme with the invention process.

The following examples are to describe the preparation of the catalysts as well as the inventive Epoxidierung, without thereby however a restriction would be to be understood.

#### Example 1

In a four-neck piston (2 l contents) 455 g Tetraethylorthosilikat were submitted and from a dropping funnel within 30 min with 15 g Tetraisopropylorthotitanat under agitating (250 rpm, sheet agitator) staggered. A colorless, clear mixture formed. Final staggered one with 800 g 20 gew. - % igen Tetrapropylammoniumhydroxid solution (alkali content < 10 ppm) and agitated still another

hour after. With 90 DEG C to 100 DEG C the alcohol mixture formed from the hydrolysis became (approx. 450 g) abdestilliert. One filled with 1,5 l deionized water up and gave the meanwhile gentle opaque sol in to 2.5 l seizing agitating autoclaves made of high-grade steel.

With a heating rate of 3 DEG /min the locked autoclave (anchor agitator, 200 rpm) became on a reaction temperature of 175 DEG C brought. After 92 hours the reaction was terminated. The reaction mixture cooled off (white suspension) was abzentrifugiert and several times with water neutrally washed. The obtained solid became dried with 110 DEG C within 24 hours (Auswaage 149 g).

Final one was burned down under air with 550 DEG C in 5 hours in zeolites still remaining Templat (calcining loss: 14 Gew. - %).

The clean-white product had Ti content of 1,5 Gew after wet-chemical analysis. - % and a content of remainder alkali below 100 ppm. The yield on used SiO<sub>2</sub> amounted to 97%. The crystallites had a large one of 0,05-0,25 µm and the product shown in the IR a typical gang with approx. 960 cm<sup>-1</sup>.

#### Example 2

1000 g Titansilikalit from example 1 5 became gew in a mixture from 6 l. - %igen sulfuric acid and 600 g 30 gew. - %iger hydrogen peroxide solution suspends and with 80 DEG C 2h long agitated. Afterwards the so treated Titansilikalit aspirated and further treated became three times as described. Afterwards the Titansilikalit in 6 l water was suspended, with 80 DEG C 2h long agitated and aspirated. This procedure was once repeated. Afterwards the so treated solid body was calcined with 150 DEG C dried and subsequent with 500 DEG C 5h long under air.

#### Example 3

950 g Titansilikalit from example 2 became in 6 l of a 1 gew. - and for 20 min under return flow cooked suspends %igen sodium acetate solution in waters, afterwards the Titansilikalit became aspirated. This procedure was still twice repeated. Subsequent one was suspended the so treated Titansilikalit in 6 l water, 30 min under return flow cooked and aspirated. Also this procedure was repeated. The Titansilikalit was then calcined with 150 DEG C dried and with 500 DEG C.

#### Example 4

100 g Titansilikalit from example 3 became with 5 g methyl cellulose drying mixed. This mixture was processed in the kneading machine under addition of 95 ml waters compressed and with a pressing power from 30 bar to strands with 2 mm in diameter. These strands were long calcined over night with 110 DEG C dried and with 500 DEG C 5h. The lateral pressure firmness of the strands without binders amounted to 9.5 N.

#### Example 5

100 g Titansilikalit from example 3 became with 5 g methyl cellulose drying mixed. This mixture became in the kneading machine under addition Kiesesol ammonium-stabilized of 70 ml waters and 12.5 g (Ludox TM AS-40, DuPont, 40 Gew. - % SiO<sub>2</sub>) compressed and with a pressing power from 30 bar to strands with 2 mm in diameter processes. These strands were long calcined over night with 110 DEG C dried and 500 DEG C 5 h. The lateral pressure firmness of the strands with 4,8 Gew. - % at binders 22.5 N amounted to.

#### Comparison example A

120 g Titansilikalit from example 3 became with 6 g methyl cellulose drying mixed. This mixture was processed in the kneading machine under addition of 40 ml waters and 60g Ludox AS-40 compressed and with a pressing power from 30 bar to strands with 2 mm in diameter. These strands were long calcined over night with 110 DEG C dried and with 500 DEG C 5h. The crush strength of the strands with 20 Gew. - % at binders 36.7 N amounted to.

#### Example 6

In 250 ml glass autoclaves became 45 ml methanol and 1.5 g of formed Titansilikalit (split with a

diameter between 0.5 mm and 1 mm) from example 4 filled and the suspension became with a magnet agitator agitated. The locked glass autoclave was pressed thereafter on -30 DEG C cooled and 20.2 g propen wurd. Afterwards the glass autoclave on 0 DEG C became heated and 32.5 g 30 gew. - were metered %ige hydrogen peroxide solution. The reaction mixture became 5 h with 0 DEG C under own pressure agitated. Afterwards the catalyst was abzentrifugiert and the content of propylene oxide by gas chromatography certain. The content of propylene oxide amounted to 7.9 Gew. - %.

#### Example 7

In 250 ml glass autoclaves became 45 ml methanol and 1.5 g of formed Titansilikalit (split with a diameter between 0.5 mm and 1 mm) from example 5 filled and the suspension became with a magnet agitator agitated. The locked glass autoclave was pressed thereafter on -30 DEG C cooled and 21.0 g propen wurd. Afterwards the glass autoclave on 0 DEG C became heated and 31.0 g 30 gew. - were metered %ige hydrogen peroxide solution. The reaction mixture became 5h with 0 DEG C under own pressure agitated. Afterwards the catalyst was abzentrifugiert and the content of propylene oxide by gas chromatography certain. The content of propylene oxide amounted to 6.9 Gew. - %.

#### Comparison example B

In 250 ml glass autoclaves became 45 ml methanol and 1.5 g of formed Titansilikalit (split with a diameter between 0.5 mm and 1 mm) from comparison example A filled and the suspension became with a magnet agitator agitated. The locked glass autoclave was pressed thereafter on -30 DEG C cooled and 20.2 g propen. Afterwards the glass autoclave on 0 DEG C became heated and 38.3 g 30 gew. - were metered %ige hydrogen peroxide solution. The reaction mixture became 5h with 0 DEG C under own pressure agitated. Afterwards the catalyst was abzentrifugiert and the content of propylene oxide by gas chromatography certain. The content of propylene oxide amounted to only 0.9 Gew. - %.

#### Comparison example C

Into 250 ml glass autoclaves did not become 45 ml methanol and 1.5 g formed Titansilikalit from example 3 filled and the suspension with a magnet agitator an agitated. The locked glass autoclave was pressed thereafter on -30 DEG C cooled and 23.2 g propen. Afterwards the glass autoclave on 0 DEG C became heated and 34.0 g 30 gew. - were metered %ige hydrogen peroxide solution. The reaction mixture became 24h with 0 DEG C under own pressure agitated. Afterwards the catalyst abzentrifugiert un the content of propylene oxide by gas chromatography certain. The content of propylene oxide amounted to 12.6 Gew. - %.

The abzentrifugierte catalyst was again abzentrifugiert with 10 ml methanol washed, and with 45 ml methanol again in the glass autoclaves filled. The locked glass autoclave was pressed thereafter on -30 DEG C cooled and 20.4 g propen. Afterwards the glass autoclave on 0 DEG C became heated and 26.0 g 30 gew. - were metered %ige hydrogen peroxide solution. The reaction mixture became 24 h with 0 DEG C under own pressure agitated. Afterwards the catalyst was abzentrifugiert and the content of propylene oxide by gas chromatography certain. The content of propylene oxide amounted to 9.6 Gew. - %.

The again abzentrifugierte catalyst was again abzentrifugiert with 10 ml methanol washed, and with 45 ml methanol again in the glass autoclaves filled. The locked glass autoclave was pressed thereafter on -30 DEG C cooled and 19.7 g propen. Afterwards the glass autoclave on 0 DEG C became heated and 31.5 g 30 gew. - were metered %ige hydrogen peroxide solution. The reaction mixture became 22.5 h with 0 DEG C under own pressure agitated. Afterwards the catalyst was abzentrifugiert and the content of propylene oxide by gas chromatography certain. The content of propylene oxide amounted to 7.8 Gew. - %.

#### Example 8

Into a double walled pressure reaction pipe from glass (inside diameter of 17 mm, length 200 mm) 10 g of catalyst strands became from example 4 filled. With a cycle pump the reactor in ascending driving fashion with methanol was flooded, whereby first 150 was driven ml the solvent into

straight passage, over possibly. to remove still adherent catalyst-deaf.

Afterwards one switched the solvent stream as recycle with a volumetric flow from approx. 5000 ml/h and cooled the reactor by means of a connected Kryostaten on a coolant temperature of approx. 0-5 DEG C.

Agent of a direct aeration agitator arranged under the supply of reactor propen became pressure-regulated with 5 to 7 bar course-drives and within an hour became over a further pump 1900 ml hydrogen peroxide (30 Gew. - % in water) the cycle methanol added.

After approximately. 3 hours the solvent analyzed became by means of a sample loop. The analysis by gas chromatography a shown content of 1,3 Gew. - % propylene oxide a corresponding yield of 0,54 mol. The solvent quantity in the circulation amounted to after reaction end approx. 3400 G.